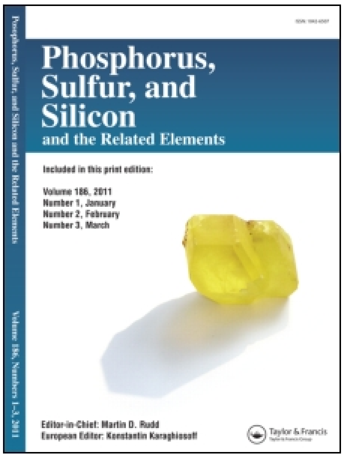

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Bruce N. Diel[a]; Arlan D. Norman[a]
[a] Department of Chemistry, University of Colorado, Boulder, Colorado

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CONVERSION OF ALLYLPHOSPHINE TO NOVEL DIPHOSPHINES: SYNTHESIS AND CHARACTERIZATION OF $CH_2{=}CHCH_2P(H)(CH_2)_3PH_2$ AND $P[(CH_2)_3]_3P$[1]

BRUCE N. DIEL and ARLAN D. NORMAN*

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

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Irradiation (λ = 300–600 nm) of gaseous $CH_2{=}CHCH_2PH_2$ in a hot-cold reactor yields the new diphosphine, $CH_2{=}CHCH_2P(H)(CH_2)_3PH_2$(I). I results from the intermolecular head-to-tail addition of phosphine PH bonds to the C=C bonds of $CH_2{=}CHCH_2PH_2$, in an anti-Markovnikov process. The AIBN-initiated radical reaction of $CH_2{=}CHCH_2PH_2$ in benzene yields PH_3 and the novel bicyclic diphosphine, $P[(CH_2)_3]_3P$(II). Characterization of I and II, based on ^{31}P, ^{1}H, and ^{13}C NMR and mass spectral data, is described.

INTRODUCTION

Primary alkenylphosphines, because of their multifunctionality (C=C, P—H and $\geqslant$P: donor) offer considerable potential for the synthesis of novel primary, secondary, or tertiary phosphines. Although several primary alkenyl phosphines have been reported previously, $CH_2{=}C(PH_2)CH_3$,[2] $CH_2{=}CHCH_2PH_2$,[3] and $C_6H_5CH{=}CHPH_2$,[4] their use in syntheses has not been exploited. Recently, we reported a highly efficient synthesis of primary alkenylphosphines of the type $CH_2{=}CH(CH_2)_nPH_2$ ($n \geq 1$),[5] which offers the opportunity for systematic development of their reaction chemistry. We have undertaken such a study of primary alkenylphosphines and we wish now to report the synthesis of two novel diphosphines, $CH_2{=}CHCH_2P(H)(CH_2)_3PH_2$(**1**) and $P[(CH_2)_3]_3P$(**2**) from one of these, allylphosphine ($CH_2{=}CHCH_2PH_2$).

RESULTS AND DISCUSSION

Photolysis of $CH_2{=}CHCH_2PH_2$

The gas-phase photolysis of $CH_2{=}CHCH_2PH_2$ in a hot-cold reactor[6] results in the slow, but high-yield formation of a head-to-tail dimer (**1**) of allylphosphine according to

$$2\,CH_2{=}CHCH_2PH_2 \xrightarrow{h\nu} \underset{\mathbf{1}}{CH_2{=}CHCH_2P(H)(CH_2)_3PH_2} \qquad (1)$$

Because **1** condenses in the cold zone of the reactor and is taken from the photolysis zone soon after formation, significant amounts of higher oligomers and/or poly-

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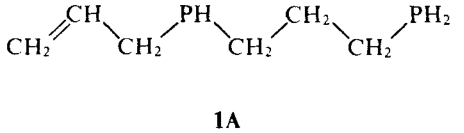
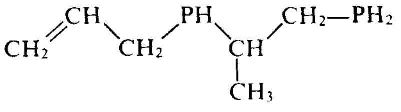
*Author to whom all correspondence should be addressed.

mers and product degradation are avoided. Typically, of the $CH_2{=}CHCH_2PH_2$ consumed, more than 85% conversion to **1** is observed. Although photolysis under other conditions, i.e. solution or standard gas phase conditions has not been examined exhaustively, the thermal gradient approach appears to be the superior mode of reaction.

Characterization of **1** as the product of head-to-tail addition of $CH_2{=}CHCH_2PH_2$ molecules is based on ^{31}P NMR, ^{1}H NMR, ^{13}C NMR, and mass spectral data. **1** exhibits a parent molecular ion at m/e 148, $C_6H_{14}P_2^+$ and a spectrum entirely consistent with that expected for a linear organophosphine.[7,8] The spectral pattern consists of ions which result from the loss of C_3H_5, $C_3H_5PH_x$, PH_x, and $C_3H_6PH_x$ moieties from the parent $C_6H_{14}P_2^+$ or various daughter ion species. ^{31}P, ^{13}C, and ^{1}H NMR spectral data support assignment of the linear structure (A) of **1** and argue against B, the Markovnikov addition product. The triplet and doublet resonances in the ^{31}P spectrum at δ-135.3 ppm and δ-70.1 ppm, respectively, confirm the presence of primary (—PH_2) and secondary (PH) phosphine moieties.[9,10] The ^{13}C NMR spectral resonances at δ-128.6 and δ-108.7 are attributable to the vinylic carbon atoms.[11,12] With the limited data available it is not possible to assign specifically the four resonances between δ-8.7 and δ-24.5 ppm; however, they are in the region characteristic of methylene carbon atoms and the observed coupling constants are within the ranges of those observed previously for one-($^{1}J_{PC}$), two-($^{2}J_{PC}$), and three-($^{3}J_{PC}$) bond phosphorus-carbon coupling constants.[24] The characteristic ABC resonance pattern[13] at δ5.8 ppm, δ5.1 ppm and δ4.9 ppm in the ^{1}H NMR spectrum (Figure 1) is assigned to the vinylic protons.[14] The doublet at δ2.4 ppm can be attributed to the allylic CH_2 group. The PH and PH_2 proton resonances are overlapping and broad, due to extensive phosphorus-proton coupling. The intense broad singlet at δ1.7 ppm (relative area 6) is assigned to the C_3H_6, methylene protons. Although the spectrum is poorly resolved in this region, the spectral pattern and peak area are consistent with that expected for a —$CH_2CH_2CH_2$—linkage. Because no resonances attributable to a CH_3 group or a CH group α to phosphorus are seen, structure **1B** containing a —$CH(CH_3)CH_2$—linkage seems unlikely.



1A



1B

Although the thermal gradient reactor results in the almost exclusive formation of allylphosphine dimer **1**, small quantities of trimer and high-molecular weight materials have been detected. It seems likely, that if the photolysis were done in a flow apparatus, where photolysis products are trapped immediately after their formation, even higher yields of **1**, with the exclusion of other products, could be achieved.

Formation of the dimer (**1**) is the result of the *anti* Markovnikov addition, possibly free radical, of a PH bond of one $CH_2{=}CHCH_2PH_2$ molecule to the C=C bond of another. Since this C=C bond is fairly unactivated this result is somewhat surprising. Photochemical initiation of PH bond additions is known to occur,[15] and may occur because tri-coordinate phosphorus derivatives absorb in the 200–220 nm region,[16] probably owing to $n \rightarrow \sigma^*$ transitions.[17] The primary step, formation of a phosphinyl radical ($R_2P\cdot$), and its subsequent addition to a C=C bond, is a widely known reaction.[18,19] Light of longer wavelength is also effective in the initiation step, if a photosensitizer is present.[15]

Allylphosphine absorbs, although not in a well defined maximum, in the 200–220

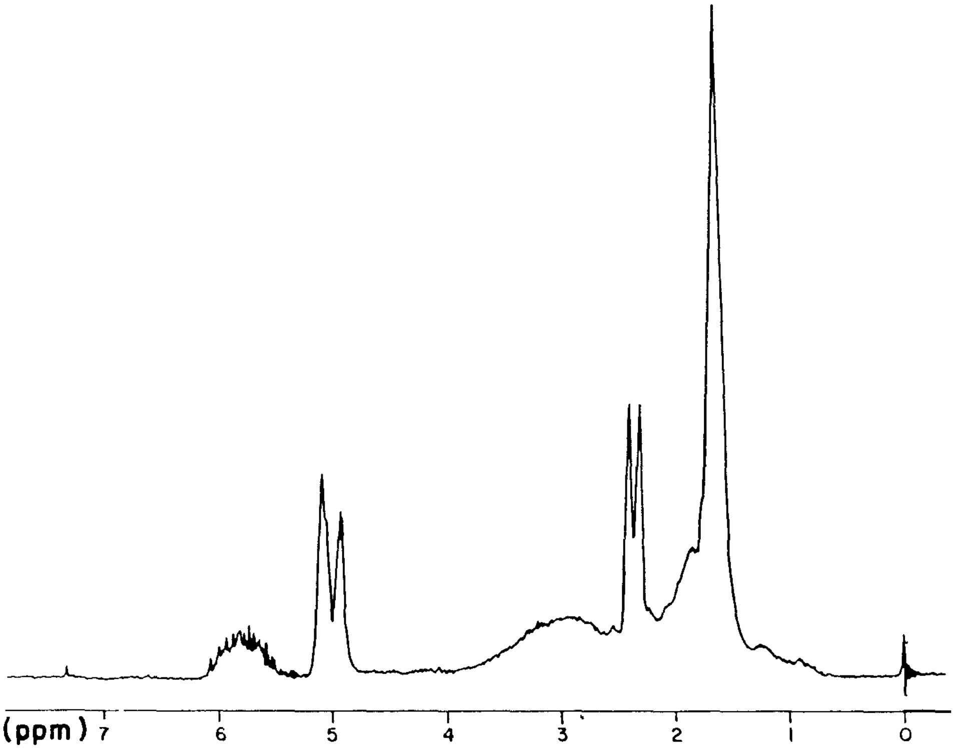
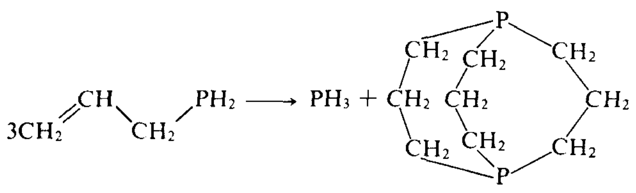


FIGURE 1 The 90.0 MHz ^1H NMR spectrum of $CH_2{=}CHCH_2P(H)(CH_2)_3PH_2$ (**1**).

nm region.[5] In the photodimerization of $CH_2{=}CHCH_2PH_2$ to **1**, the photochemical homolysis of a P—H bond seems unlikely, in view of the source employed. The Pyrex jacketed lamp transmits only slight irradiation below 300 nm.[20] It seems likely that the reaction may involve a photosensitizer or another free radical source. Trace amounts of Hg (a known photosensitizer)[20] or $CH_2{=}CHCH_2Br$, from which the phosphine is prepared, cannot be excluded. It is known that formation of allyl radicals occurs upon irradiation of allyl halides above $\lambda > 250$ nm.[21] Further studies to elucidate this interesting mechanistic problem are planned.

AIBN Initiated Reactions

Treatment of allylphosphine in benzene solvent with a radical initiator, such as AIBN [AIBN = azo-2,2′-bis(isobutyronitrile)], results primarily in formation of PH_3 and the new cage diphosphine 1,5-diphosphabicyclo[3.3.3]-undecane (**2**). The reaction stoichiometry is as shown in Eq. 2. Small quantities of $(CH_2{=}CHCH_2)_3P$,

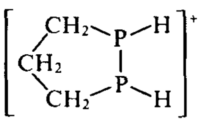


(2)

2

$(CH_2{=}CHCH_2)_2PH, CH_2{=}CHCH_3$ and the previously reported $H\overline{PCH_2CH_2CH_2P}H$[7] are observed also. Clearly, the products formed here are unique and quite different from those observed under gas-phase photolysis conditions. No **1** was detected; likewise, no **2** was detected among the photolysis products discussed above.

Characterization of **2** as a new diphosphine rests on ^{31}P, ^{13}C, ^{1}H NMR and mass spectral data. The mass spectrum of **2** is surprising, and not simply interpretable, since a parent ion at m/e 188 is not observed. The highest-mass peak occurs at m/e 154, assigned to the $^{12}C_9H_{15}P^+$ ion. This ion corresponds to the $P[(CH_2)_3]_3P^+$ parent minus a PH_3 molecule. Even at lower ionizing voltages, e.g. 20 and 30 eV, no parent ion appears. The mass spectrum of **2** closely resembles that of $(CH_2{=}CHCH_2)_3P$, except that ions at m/e 33, 34, 52, 74 and 106 are observed. The m/e 33 and 34 peaks likely arise from PH_3, formed in the inlet as a result of highly efficient PH_3 elimination from ionized **2**. The m/e 106 peak, uniquely attributable to $^{12}C_3H_8P_2^+$



may have a cyclic structure and may be the only ion arising unambiguously from the highly unstable, but not observed, two-phosphorus ions of **2**.

NMR spectral data establish clearly the cage type structure of **2**. The ^{1}H NMR exhibits a complex, narrow resonance centered ca. $\delta 1.4$ ppm (Figure 2), in a region characteristic of aliphatic CH_2 groups, located α and β to phosphorus atoms.[22,25]

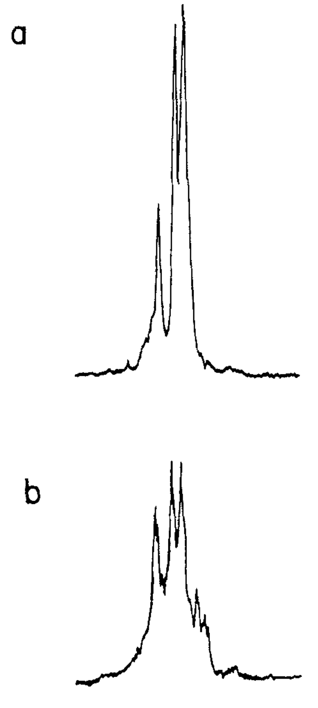


FIGURE 2 The 100.0 MHz ^{1}H NMR spectrum of $P[(CH_2)_3]_3P$; with (a), and without (b) ^{31}P-decoupling.

Particularly important to note, there are no protons in vinylic or allylic regions to be seen.[13,14] The ^{31}P NMR spectrum shows but one resonance at δ-28.2 ppm, a position characteristic of trialkylphosphines with three or four carbon linear substituent chains.[23-25] The ^{13}C NMR spectrum exhibits two resonances, in a two to one area ratio at δ-30.00 ppm and δ-30.34 ppm, which are assigned to carbon atoms in positions α and β to the phosphorus atoms, respectively.[24,25] Upon ^1H decoupling, the resonances collapse to apparent triplets of $J = 15.6$ Hz and $J = 4.9$ Hz, respectively. This pattern requires that the $|{}^1J_{^{31}P-^{13}C}|$ and $|{}^3J_{^{31}P-^{13}C}|$ coupling constants be closely similar in magnitude; however, this is a common occurrence in organophosphines.[9,24,25,26] The coupling constants are closely similar to those seen in general in organophosphines with aliphatic substituents.[24] Based on these comparisons, the triplet with apparent J of 4.9 Hz is assigned to the β—CH_2 units, and the triplet with J of 15.6 Hz is assigned to the α—CH_2 units.

The mechanism by which PH_3 and **2**, as major products, and $(CH_2{=}CHCH_2)_3P$, $(CH_2{=}CHCH_2)_2PH$, $CH_2{=}CHCH_3$ and $H\overline{PCH_2CH_2CH_2P}H$, as minor products, form in the AIBN initiated reaction of $CH_2{=}CHCH_2PH_2$ is complex; however, from ^{31}P NMR spectra collected as the reaction progresses, some indication of the most important processes is obtained. After heating for 3 min. at 100°C, the spectrum in Figure 3a is seen. Resonances due to unreacted $CH_2{=}CHCH_2PH_2$(A, δ-132.9 ppm), PH_3(B, δ-200 ppm), **2** (C, δ-28.2 ppm) and a secondary phosphine[9] (D, δ-70.1 ppm) are present. Of particular importance is the already relatively high concentration of PH_3 in the system. The inverted, out-of-phase peaks are assigned to the polarized resonances of radical species in the reaction (CIDNP).[27] Only rarely are these seen during the course of the reaction, a phenomena suggesting unusually long-lived radical species in the system.[28] After an additional 10 min. at 100°, spectrum 3b is obtained. Consumption of $CH_2{=}CHCH_2PH_2$(A) is nearly complete. Resonances from PH_3(B) and **2**(C) predominate; the doublet at D has decreased in relative area. A small singlet at δ-34.3(E), due to $(CH_2{=}CHCH_2)_3P$, is now present. Proton decoupling verified the multiplicity assignments of peaks A–D.

The observed spectral data allow some limited mechanistic conclusions. Phosphine forms easily and in substantial quantities early in the reaction. In addition, a secondary phosphine (peak D) forms early. Although precedence might suggest the addition of a $CH_2{=}CHCH_2\dot{P}H$ species to the C=C bond of another $CH_2{=}CHCH_2PH_2$ molecule, an alternate preferred route is supported by the data. Reversible reaction of $CH_2{=}CHCH_2\dot{P}H$ with $CH_2{=}CHCH_2PH_2$, according to Eq. 3 might form

$$CH_2{=}CHCH_2PH\cdot + CH_2{=}CHCH_2PH_2 \rightleftharpoons \underset{\mathbf{4}}{(CH_2{=}CHCH_2)_2\dot{P}} + PH_3 \quad (3)$$

the PH_3 and **4**, a species key to later reaction processes. Reaction in Eq. 3 is entropically favored and is supported by the rapid formation of PH_3. Species **4** could then participate further in a variety of reactions, e.g.

$$\mathbf{4} + H_2C{=}CHCH_2PH_2 \rightleftharpoons \underset{\mathbf{5}}{(H_2C{=}CHCH_2)_2PH} + \underset{\mathbf{6}}{H_2C{=}CHCH_2\dot{P}H} \quad (4)$$

Such a process allows for radical chain propagation via **6**. The doublet at δ-70.1 ppm (D) in Figure 1a is tentatively assigned to **5**. Another likely fate for the secondary phosphinyl radical **4** is its addition to a C=C bond, i.e.

$$\mathbf{4} + H_2C{=}CHCH_2PH_2 \rightleftharpoons \underset{\mathbf{7}}{(H_2C{=}CHCH_2)_2PCH_2\dot{C}HCH_2PH_2} \quad (5a)$$

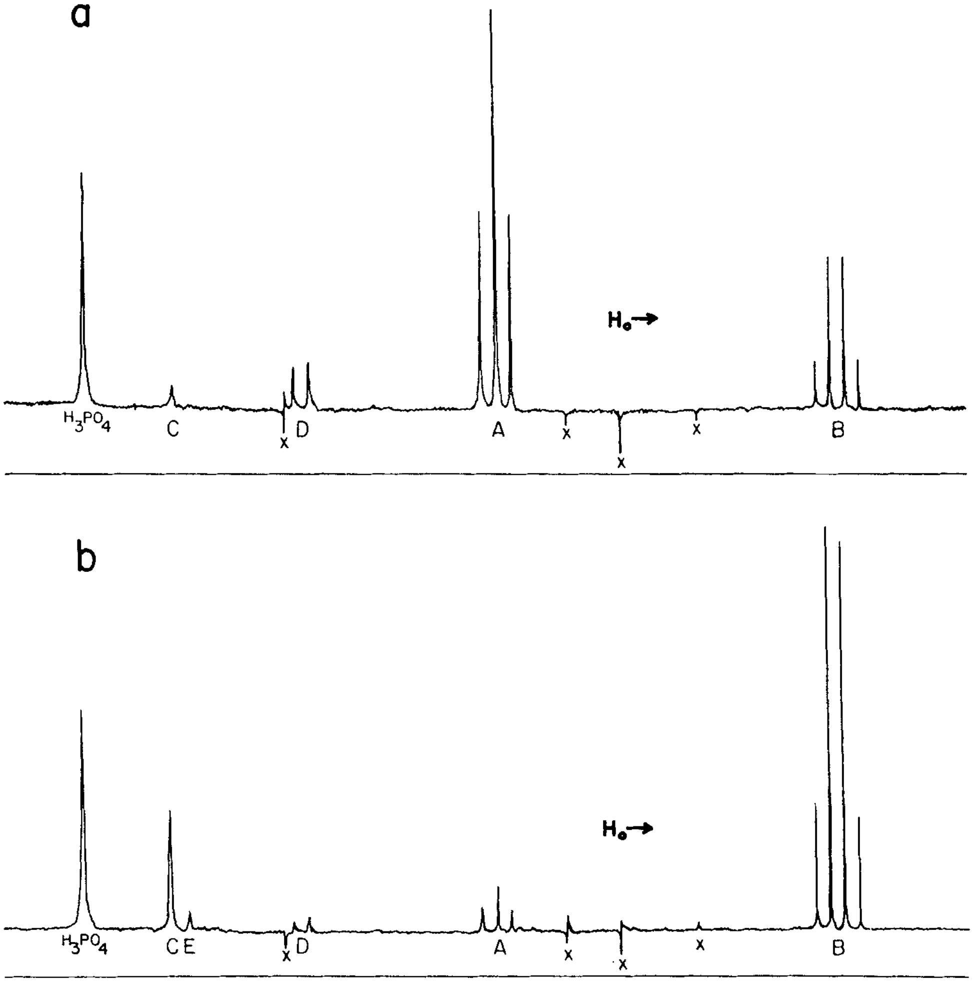
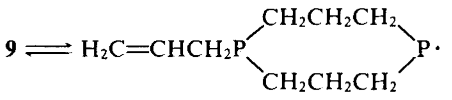


FIGURE 3 The ^{31}P NMR spectrum of AIBN promoted reaction of $CH_2{=}CHCH_2PH_2$ after; (a) 3 min. at 100°C and (b) 10 min. at 100°C. Inverted resonances (CIDNP) resonances are marked by an *x*. Resonances (δ, ppm): H_3PO_4, 0.0; A, −132.9; B, −200.0; C, −28.2; D, −70.1; and E, −34.3.

$$\mathbf{7} + H_2C{=}CHCH_2PH_2 \rightleftharpoons \mathbf{6} + \underset{\mathbf{8}}{(H_2C{=}CHCH_2)_2P(CH_2)_3PH_2} \qquad (5b)$$

Although ^{31}P NMR spectral evidence for **8** was not obtained, its formation provides a logical precursor to the bicyclic di(tertiary) phosphine **2**, as shown below.

$$\mathbf{4} + \mathbf{8} \rightleftharpoons \mathbf{5} + \underset{\mathbf{9}}{(H_2C{=}CHCH_2)_2P(CH_2)_3\dot{P}H} \qquad (6a)$$



$$\mathbf{9} \rightleftharpoons H_2C{=}CHCH_2P\begin{matrix}CH_2CH_2CH_2\\ \\ CH_2CH_2CH_2\end{matrix}P\cdot \qquad (6b)$$

10

$$\mathbf{10} + H_2C{=}CHCH_2PH_2 \rightleftharpoons \mathbf{6} + \underset{\mathbf{11}}{H_2C{=}CHCH_2P[(CH_2)_3]_2PH} \qquad (6c)$$

A subsequent intramolecular P—C bond formation reaction, similar to Eq. 6b, involving **11** results in the formation of $P[(CH_2)_3]_3P$, **2**. Further study of the mechanism by which **2** is formed, including a study of the CIDNP resonances will be the subject of a future report.

The two new diphosphines reported herein offer interesting potential for further study. Both should coordinate metals, to form complexes with novel and/or useful properties. **1**, if substituted at PH positions could lead to new chiral diphosphines, of interest in asymmetric synthesis. **2**, because of the unique arrangement of P atoms to one another, may lead to novel structural problems, perhaps not unlike those reported for the related $N[(CH_2)_3]_3N$ type systems.[29]

EXPERIMENTAL

Apparatus and Materials.

All manipulations were carried out in standard vacuum line apparatus.[6] Infrared spectra (4000–400 cm^{-1}) were obtained using a Perkin Elmer Model 467 spectrophotometer. Mass spectra were obtained using a Varian MAT CH-5 spectrometer. ^1H NMR spectra were obtained with Varian EM 360 (60.0 MHz) and EM 390 (90.0 MHz) spectrometers. Phosphorus-31 NMR and ^{13}C NMR spectra were obtained with a JEOL PFT 100 spectrometer equipped with standard probe accessories. ^1H and ^{13}C chemical shifts were measured relative to internal $(CH_3)_4Si$ and ^{31}P shifts were measured relative to 85% H_3PO_4. ^{31}P and ^1H chemical shifts measured downfield from the standard are given positive ($+\delta$) values. ^{31}P, ^{13}C, and ^1H NMR chemical shifts are given to ±0.2, ±0.2, and ±0.05 ppm, respectively. All photolysis experiments were carried out using a Pyrex-jacketed low pressure mercury lamp (General Electric) with principal light emission in the range 300 nm to 600 nm.

Allylphosphine was prepared and purified as described previously.[5] AIBN [azo-2,2′-bis(isobutyronitrile)] from Matheson, Coleman, and Bell was used as obtained. Benzene and toluene were distilled from sodium-lead alloy prior to use. $CDCl_3$ (Stohler Isotope Chemicals) was purified by fractional condensation prior to use.

Reaction materials from the reactions below were characterized by comparison of their physical and/or spectral properties with those in the literature or with spectra of samples prepared independently in our laboratories. Mass spectral data, refer to the most-intense peak in the envelope in question.

The organophosphines described in this study, including **1** and **2**, prepared for the first time herein, are *highly malodorous* and probably *highly toxic*. Consequently, great care and prudence should be exercised in their handling. Handling in other than a high-vacuum system is not recommended.

Photolysis of Allylphosphine. Synthesis of $CH_2{=}CHCH_2P(H)CH_2{-}CH_2CH_2PH_2$(**1**).

Typically 20 mM of $CH_2{=}CHCH_2PH_2$ was condensed into a 600 ml thermal gradient quartz bulb reactor equipped with an 8 cm. condensation cold-finger. During photolysis the cold-finger was maintained at 0°, by an ice bath. Bulk allylphosphine condensed at 0°C (0° vp = 98 mm). The cold-finger was wrapped with black tape to prevent photolysis of the bulk allyl-phosphine or the initially-formed photoproducts. During photolysis the bulb was air-cooled to prevent the bulb temperature from rising significantly above ambient. After 50–60 hr. of exposure to sunlamp irradiation in the reactor, volatile materials were removed and passed through traps at −45°C and −160°C into a −196°C trap. No noncondensible gases were observed and only trace quantities of PH_3 were collected at −196°C. The −160°C trap contained unreacted $CH_2{=}CHCH_2PH_2$; typically 15–20% conversion occurred in 50–60 hr. The −45°C trap contained $CH_2{=}CHCH_2P(H)(CH_2)_3PH_2$ (**1**), along with small quantities of higher-molecular weight organophosphine oligomers, characterized tentatively by mass spectral data. Owing to the difficulties associated with handling the low-volatility, malodorous higher oligomers, they were not studied further. Typically, yields of **1** between 80–85%, based on the $CH_2{=}CHCH_2PH_2$ which reacted, were obtained. Low-temperature fractional distillation[6] of material in the −45°C trap yields pure **1**. The room temperature vapor pressure of **1** is <0.1 torr; **1** freezes to a glass at ca. −50°C. *Spectral Data:* Mass spectrum: The most intense peak of the parent and eight most intense ion envelopes occur at (relative intensities in parentheses) 146(91), 105(100), 77(38), 73(32), 63(17), 57(25), 43(36), 41(80) and 39(57); parent ion, $^{12}C_6H_{14}P_2$, at m/e 148(4). ^{31}P NMR spectrum ($CDCl_3$): δ–70.1 ppm (area 1, d, $^1J_{PH} = 195.3 \pm 2.4$ Hz) and δ–135.3 ppm (area 1, t, $^1J_{PH} = 190.4 \pm 2.4$ Hz. ^{13}C NMR spectrum [in $(CH_3)_4Si$]: δ–128.6 ppm (area 1, s), δ–108.7 ppm (area 1, d, $^3J_{CP} = 6.1 \pm 1.2$ Hz), δ–24.5 ppm (area 1, d, $J_{CP} = 11.0 \pm 1.2$ Hz), δ–18.7 ppm (area 1, d, $J_{CP} = 12.2 \pm 1.2$ Hz) δ–13.6 ppm (area 1, d, $J_{CP} = 7.3 \pm 1.2$ Hz), and δ–8.6 ppm (area 1, d, $J_{CP} = 6.1 \pm 1.2$ Hz). ^1H NMR spectrum (in $CDCl_3$, Figure 1): δ5.8 ppm (area 1, complex multiplet), δ5.1 (area 1, complex), δ3.0 ppm (area 3, unresolved, broad), δ2.4 ppm (area 2, $^2J_{PH}$ 7.50 ± 0.1 Hz) and δ1.7 ppm (area 6, s).

AIBN Initiated Reaction of Allylphosphine. (A) Synthesis of $P[(CH_2)_3]_3P$(**2**).

Under N_2, ca. 0.1 mM AIBN in 10 mL benzene was loaded into a 100 mL reaction vessel equipped with a break seal and ground joint for vacuum line connection. After freeze-thaw degassing the benzene solution, 19.7 mM $CH_2{=}CHCH_2PH_2$ was condensed into the vessel, the reactor sealed, the reaction vessel was allowed to warm temperature and then heated to 100°C. After 30 min. the tube was opened and N_2 was removed. Volatile reaction materials were passed through traps at −78°C, −130°C, −160°C and −196°C. The −196°C trap contained only PH_3 (4.9 mM, confirmed by IR spectrum). The −160°C trap contained ca. 1.8 mM $CH_2{=}CHCH_3$ and 0.2 mM $CH_2{=}CHCH_2PH_2$, (estimated from IR spectral intensities). Additional unreacted $CH_2{=}CHCH_2PH_2$, 2.0 mM, condensed at −130°C. Low-temperature fractional distillation of the −78°C condensate resulted in the isolation of benzene solvent, ca. 0.2 mM $HPCH_2CH_2CH_2PH$ (**3**),[7] ca. 0.5 mM $(CH_2{=}CHCH_2)_3P$ (confirmed by ^1H and ^{31}P NMR and mass spectra), and ca. 4.7 mM $P[(CH_2)_3]_3P$(**2**). The vapor pressure of **2** at 25°C is <0.5 torr; **3** freezes to a glass.

Spectral Data: Mass spectrum: The most intense peak in the eleven most intense mass spectral envelopes occurs at m/e (relative intensities in parentheses): 154(5), 126(9), 113(8), 106(5), 84(39), 74(32), 71(18), 57(20), 45(25), 41(100), and 34(38). No parent ion was observed. ^{31}P NMR spectrum (in C_6D_6): δ–28.2 ppm(s). ^{13}C NMR spectrum (in C_6D_6): δ–30.0 ppm (area 1, t, $^2J_{PC} = 4.9$ Hz) and δ–30.3 ppm (area 2, t, $^{1,3}J_{PC} = 15.6$ Hz). ^1H NMR spectrum (in C_6D_6), Figure 2): δ1.4 ppm (complex multiplet); ^{31}P decoupled, maxima at δ1.44 ppm, δ1.38 and δ1.34 ppm. Owing to the highly malodorous nature of **1** and **2**, infrared spectra were not obtained.

(B) ^{31}P *NMR Spectrally Monitored Reactions.*

Typically, a dry NMR tube was charged with 0.07 mM AIBN, the tube was attached to a vacuum line, $CH_2{=}CHCH_2PH_2$ (2.4 mM) and 5-6 mM of C_6D_6 were condensed into the tube, and the tube sealed. The tube was heated to 100°C; gas evolution was evident immediately. After measured periods of time, the tube was cooled to 25°C (and the ^{31}P NMR spectrum obtained. Spectra after 3 min and 10 min at 100°, are shown in Figure 3a and 3b, respectively.

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REFERENCES AND NOTES

1. Taken in part from the Ph.D. thesis of Bruce N. Diel, University of Colorado, 1980.
2. H. Goldwhite, *J. Chem. Soc. A.* 3901 (1965).
3. S. Chan, H. Goldwhite, H. Keyzer, D. G. Rowsell and R. Tang, ***Tetrahedron*, 25,** 1697 (1969).
4. (a) G. M. Bogolyubov and A. A. Petrov, ***Zhur. Obsch. Khim.*, 33,** 3774 (1963); (b) B. I. Ionin, G. M. Bogolyubov and A. A. Petrov, ***Russ. Chem. Rev.*, 36,** 249 (1967).
5. B. N. Diel, R. H. Shay, M. L. Thompson and A. D. Norman, submitted for publication.
6. D. F. Shriver, "The Manipulation of Air-Sensitive Compounds," McGraw-Hill, New York, N.Y., 1969.
7. K. Issleib and D. Thorausch, ***Phosphorus and Sulfur*, 4,** 137 (1978).
8. M. Halman, *J. Chem. Soc.*, 3270 (1962).

9. M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. Van Wazer, *Topics in Phosphorus Chemistry*, Vol. 5, M. Grayson and E. J. Griffith, Eds., John Wiley, New York, 1967.
10. S. O. Grim, W. L. Briggs, R. C. Barth, C. A. Tolman and J. P. Jesson, *Inorg. Chem.*, **13**, 1095 (1974).
11. L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," John Wiley and Sons, Inc., New York, N.Y., 1972.
12. G. C. Levy and G. L. Nelson, "Carbon-13 NMR for Organic Chemists," Wiley Interscience, New York, N.Y., 1972.
13. R. A. Abrahams, "Analysis of High-Resolution NMR Spectra," Elsevier Publishing Co., Amsterdam, 1974.
14. A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1969).
15. A. R. Stiles, F. F. Rust and W. E. Vaughn, *J. Am. Chem. Soc.*, **74**, 3282 (1952).
16. (a) M. Hallman, *J. Chem. Soc.*, 2853 (1963); (b) B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N.Y., 1969.
17. R. Rao, "Ultraviolet and Visible Spectroscopy," Butterworth's Scientific Publications, London, 1961.
18. (a) M. M. Rauhut, H. A. Currier, A. M. Semsel, V. P. Wystrach, *J. Org. Chem.*, **26**, 5138 (1961); (b) D. L. Dubois, W. H. Myers and D. W. Meek, *J. Chem. Soc., Dalt. Trans.*, 1011 (1975); (c) V. V. Penkovskii, *Russ. Chem. Rev.* (*Eng. Trans.*), 449 (1975).
19. C. Walling and M. X. Pearson, *Topics in Phosphorus Chemistry*, Vol. 3, M. Grayson and E. J. Griffith, Eds., John Wiley, New York, 1966, Chapter 1.
20. W. A. Noyes, S. and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N.Y., 1941.
21. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley Interscience, New York, N.Y., 1966.
22. G. Mavel, *Prog. NMR Spectr.*, **1**, 251 (1966).
23. E. Fluck and J. Lorenz, *Z. Naturforsch.*, **22B**, 1095 (1967).
24. B. E. Mann, *J. Chem. Soc. Perkin II*, 30 (1972).
25. P. W. Clark, J. L. S. Curtis, P. E. Garrow and G. E. Hartwell, *Can. J. Chem.*, **52**, 1714 (1974).
26. S. L. Manatt, G. L. Juvinall and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 2664 (1963).
27. (a) S. H. Pine, *J. Chem. Ed.*, **49**, 664 (1972); (b) H. R. Ward, *Accts. Chem. Res.*, **5**, 18 (1972).
28. Y. A. Levin, A. V. Ilyasov, D. G. Pobedimiskii, E. I. Goldfarb, I. I. Saidashev and Y. Y. Samitov, *Izvest. Akad. Nauk. SSSR. Ser. Khim.*, **7**, 1680 (1970).
29. R. W. Alder, N. C. Goode, T. J. King, J. M. Mellor and B. W. Miller, *J. Chem. Soc. Chem. Comm.*, 173 (1976).